

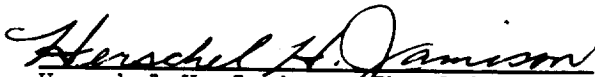
DETERMINATION OF COMPATIBILITY
OF VARIOUS POLYMERS USED IN
THE APOLLO SPACECRAFT WITH A
MIXTURE OF UNSYMMETRICAL DIMETHYL
HYDRAZINE, HYDRAZINE AND
NITROGEN TETROXIDE VAPORS

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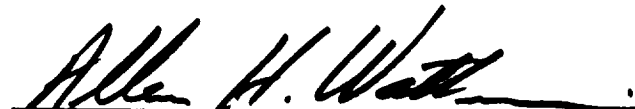
DETERMINATION OF THE COMPATIBILITY OF VARIOUS POLYMERS USED IN
THE APOLLO SPACECRAFT WITH A MIXTURE OF UNSYMMETRICAL DIMETHYL HYDRAZINE,
HYDRAZINE AND NITROGEN TETROXIDE VAPORS

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INTRODUCTION

The purpose of this test program was to determine the effects on the serviceability of various polymers and elastomers used in the Apollo spacecraft when exposed to a mixture of the vapors from Aerozine-50 (50-50 blend of unsymmetrical dimethyl hydrazine and hydrazine) and nitrogen tetroxide. Also to be determined was the extent of reaction between the propellant vapors as indicated by chemical analyses as well as temperature and pressure rise upon mixing. The test program was conducted by the Thermochemical Test Branch Materials Laboratory for the Primary Propulsion Branch of the Propulsion and Power Division. It was conducted at the Materials Laboratory compatibility facility located at building 1151, Ellington Air Force Base, Texas, and at building 356 in the Thermochemical Test Branch, MSC, Houston, Texas. The test was completed November 6, 1966.

DESCRIPTION OF TEST SPECIMENS

The following is a list of spacecraft materials tested in this program along with the specific types used and their sources. Also given is some of the basic chemistry pertaining to these materials.

1. Kel-F Film - 3M Company, Type 82, Fed. Spec. L-P385A, Grade 2
2. Silicone Rubber - DuPont, MIL-R-5847G, Class 2A, Grade 70, sheet form.
3. Butyl Rubber - Stillman Rubber Co., SR634-70, Batch 58580. This material was in the form of O-rings.
4. Teflon - DuPont, sheet form.
5. Mylar - DuPont, sheet form.

The specimens were cut into coupons approximately 2 inches by 4 inches and cleaned and dried before testing. Initial weights and thicknesses were recorded before testing.

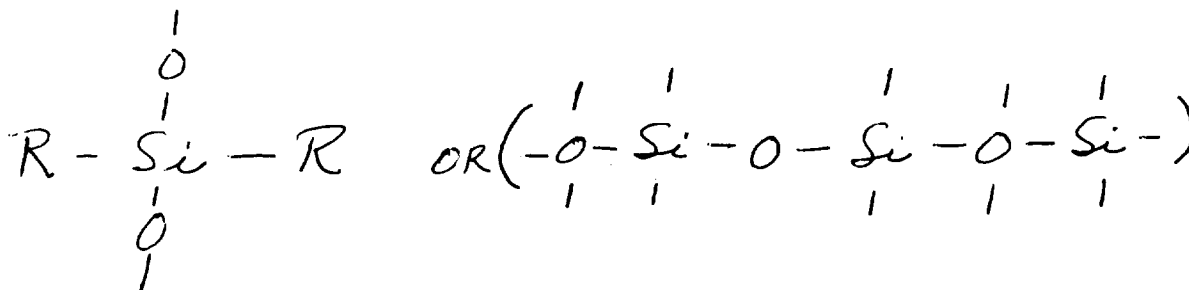
Kel-F

This material is a close relative of Teflon since the only difference in molecular structure is that one of the four fluorine atoms in the Teflon monomer has been replaced by a chlorine atom producing chlorotrifluoroethylene, $CF_2 = CFCl$. It is a high molecular weight thermoplastic to which fluorine contributes a high order of thermal and chemical stability while chlorine provides rigidity at room temperature and fluidity in the melt.

Many of the physical and chemical properties of the material are related to the degree of crystallinity which, in turn, is due to the rapidity of the cooling process following molding or extrusion of the final product, i.e. quick quenched product has the least crystallinity and is the least rigid. Chemically, chlorotrifluoroethylene is highly resistant to the attack of strong acids, alkalis, oxidants and solvents. There is no known solvent for the material at room temperature. Its dielectric loss factor, though excellent, is not as good as the loss factor for Teflon.

Silicone rubbers

This polymer is closely related to a large number of materials resembling oils, greases, putty and rubber in which the usual building block, the carbon atom, has been replaced by silica in the following configuration:



It is readily seen that the open bonds at the oxygen atoms are positions of attachment for other similar radicals and thus long chains are produced, giving a "rubbery" consistency. Compounds like this, having the general formula $H_3Si(OSiH_2)_nOSiH_3$, are called siloxanes.

These polymers are characterized by a unique combination of properties. They are stable, serviceable over a wide span of temperatures, water repellent and resistant to oxidation and weathering. They retain good physical and dielectric properties in severe operating conditions.

Butyl Rubber

Butyl rubber is produced by the polymerization of isobutylene, $\{(CH_3)_2C=CH_2\}$, and a diolefin such as isoprene, $\{(CH_2)=C(H)-C(CH_3)=C(H)\}$, at $-125^{\circ}F$ to $-150^{\circ}F$ in the presence of a Friedel-Crafts catalyst. Butyl rubber, though difficult to vulcanize, exhibits certain extraordinary characteristics such as low gas permeability, high gum tensile strength, resistance to oxidation, resistance to strong bases and strong acids and resistance to swelling by certain oils which makes it a superior material for specialized spacecraft and life support applications.

Butyl rubber has some weaker characteristics, especially in cold temperature applications such as cold buckling and poor resilience, as compared to some other types of elastomers. However, when used in conjunction with other elastomers to supplement these weak areas, butyl rubber performs outstandingly.

Teflon

This product is a polymer derived from tetrafluoroethylene, C_2F_4 . When tetrafluoroethylene is polymerized, it becomes polytetrafluoroethylene commonly called Teflon. It is a highly crystalline, linear polymer, unique among organic compounds in its chemical inertness, stability at high temperatures, and extremely low dielectric loss factor.

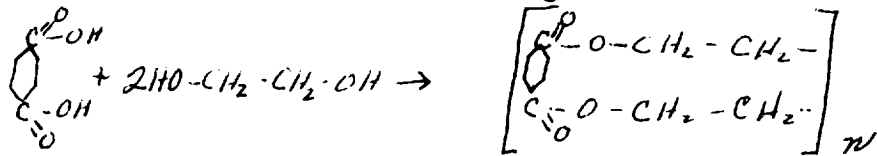
Under most conditions, the chemical resistance of polytetrafluoroethylene is equal to or superior to any known engineering material including metals, ceramics, plastics, or vitrics. This is due to the presence of fluorine in the molecule. It is inert to nearly all chemicals and solvents normally used. An exception to this are the alkali metals. Only at elevated temperatures and pressures will this material be affected by solvents and highly reactive chemicals such as halogens and halogenated compounds.

This polymer does not become fluid at its melting point ($327^{\circ}C$) but is, rather, a highly viscous liquid, (viscosity approximately 10 poises). This characteristic greatly enhances the engineering characteristics.

Mylar

Chemically, Mylar is polyethylene terephthalate which is a member of the polyester resin family. It is usually produced by reacting ethylene glycol

with terephthalic acid in the following manner:



Physically, the resulting polymer has a melting point of 265°C and a second order transition temperature of 70° to 80°C. When produced as a film, this material has a highly oriented molecular structure characterized by high tensile strength, good electrical resistance and good resistance to moisture. It is normally useful in a temperature range from -60°C to 150°C. It is used for electrical insulation and as a barrier to moisture.

Due to the double bonding in the polymer chains and to the oxygen linkage, Mylar is not a very stable material when subjected to extreme conditions. From a study of the molecular structure, it could be predicted that Mylar would not withstand sustained exposure to the highly reactive hypergolic propellants.

DESCRIPTION OF CHEMICAL ENVIRONMENT

The test specimens were subjected to a chemical vapor environment composed of a mixture of unsymmetrical dimethylhydrazine/hydrazine (A-50), nitrogen tetroxide and helium. This mixture ratio was roughly equal between the A-50 and nitrogen tetroxide and had a high concentration of helium since it was the pressurant gas used. This mixture was chosen in order to simulate a hypothetical condition which might occur within spacecraft propellant lines due to valve and regulator leakage. Thus the results of materials exposure to this synthetic mixture is valuable in determining the reliability of certain spacecraft materials which might be subjected to the prescribed conditions.

DESCRIPTION OF TEST APPARATUS

A 304 type stainless steel reaction vessel was used to subject the various samples to the vapor mixture. This vessel was of simple design being composed of a cylinder, which was 9 inches deep by 4 inches diameter with a detachable lid. This lid was equipped with a visual reading pressure gage and a thermocouple for temperature measurement. Provision also was made for providing a temperature regulation up to 150°F with a water bath.

In addition to the reaction vessel, the assembly was composed of an oxidizer (N_2O_4) pressurization tank and a fuel (A-50) pressurization tank, each of these vessels were also equipped with a water bath. These propellant tanks were equipped to contain the required pressurization of 210 psi. All three vessels were plumbed together in such a way as to allow quantitative regulation of gas flow from the propellant tanks into the reaction vessel through solenoid valves. It will be noted from Figure 1 that a helium pressurization bottle was attached to the propellant tanks. This was to provide the required pressure for transport as well as the dilution of the propellant vapors to simulate possible spacecraft conditions within the transfer lines. See Figure 1 for schematic details.

In summary, the equipment may be listed as follows:

A. Reaction Vessels

1. 304 stainless steel cylinder with detachable lid and Teflon gasket. Dimensions were 4 inch inside diameter with a 9 inch depth. The reaction vessels are equipped with a pressure gage and a thermocouple for temperature indication.

B. Water bath for reaction vessels

C. Pressure vessels for Aerozine-50 and nitrogen tetroxide. Each vessel and associated plumbing is equipped with:

1. Pressure gage
2. Metering valve
3. Solenoid valve
4. Check valve
5. Separate helium supply and connection
6. Thermocouple for temperature indication
7. Water bath with heaters and thermostat

TEST PROCEDURE

Separate tanks containing N_2O_4 and A-50 were pressurized to 210 psi with separate helium sources and heated to 150°F. A coupon of the test material was placed in the stainless steel reactor vessel. N_2O_4 and A-50 vapors were metered to give equal flow rates to produce a final pressure of 185 psia. The vessels were stored in a 150°F water bath for the prescribed period. At the end of the test periods, the samples were removed, examined and measured. The tests were conducted, in an identical manner, three times in order to study the effects of time (1, 5 and 10 days) on the outcome.

The following is the stepwise procedure:

- A. Two coupons of each test material were placed in a clean reaction vessel.
- B. The reaction vessel was then sealed and purged with helium.
- C. The reaction vessel was placed in the water bath at 150°F.
- D. Aerozine-50 was added to one pressure vessel until approximately one-third full. Nitrogen tetroxide was added to the other pressure vessel until approximately one-half full.
- E. The supply tanks were placed in the water baths. When the vapors of the A-50 and N_2O_4 reached a temperature of 150°F, both supply tanks were pressurized to 210 psig by bubbling helium through the liquid.
- F. The reaction vessel was connected to both the A-50 and N_2O_4 supply tanks. Both solenoid valves were simultaneously activated admitting A-50 vapors and N_2O_4 vapors at equal flow rates into the reaction vessel until a pressure of 185 psig was obtained.
- G. The reaction vessel was disconnected from the supply tanks and placed in the water bath at 150°F for the test duration.
- H. At the end of the test period, the final pressure in the reaction vessel was recorded.
- I. Both test specimens were removed. One specimen was water washed and dried; the other specimen was dried without washing.
- J. Final weights and thicknesses of the test specimens were measured. Visual observations were also made and recorded. See Table I for data summary.

RESULTS AND DISCUSSION

Preliminary calculations indicated that the vapor mixture in the reaction vessel would be predominantly composed of helium and nitrogen tetroxide with Aerozine-50 making up a minor portion. The explanation, of course, is based on the relative partial pressures of each of the ingredients; at 150°F, the vapor pressure of nitrogen tetroxide is 91.1 psia while that of Aerozine-50 is 12.5. It was noted, however, that the Aerozine-50 content did not show up as a 50:50 mixture of UDMH and hydrazine but rather showed that the UDMH had vaporized leaving the hydrazine behind, thus only the UDMH was found; this is due to the much higher partial pressure of UDMH over hydrazine.

From Table I, it will be seen that a significant temperature differential was measured upon the initial addition of the vapors to the tanks. These temperature readings are somewhat erratic which is probably due to inadequate control over and measurement of the conditions rather than indicating a significant difference in the true temperatures within the vessel. Since the temperature increases for the actual tests, which included the propellant vapors, was of similar magnitude to the increases in those tests with helium alone, it appears that the chemical reaction between the vapors was small. Apparently the temperature rise, as far as this test reveals, is due mainly to the increase in pressure rather than a chemical reaction between the oxidizer and fuel vapors.

As evidenced by Table II, the effects of the test environments on the specimens were very severe and only the fluorinated compounds (Kel-F and Teflon) were able to endure to any significant extent.

CONCLUSIONS

Vapors of nitrogen tetroxide and unsymmetrical dimethyl hydrazine and hydrazine (A-50) diluted with helium do not undergo a rapid reaction even under elevated temperatures (250°F) and pressure (200 psi). Chemical analysis, performed by mass spectrometer techniques, of the original mixture compared with the mixture after several days indicates a slow chemical reaction; many intermediate species appear which, apparently have never been extensively studied. (A study of these intermediate species would perhaps answer some of the questions regarding the hypergolicity of these propellants).

The results of this test project indicates that prolonged exposure to nitrogen tetroxide-Aerazine-50 vapors severely alters the appearance as well as the physical and chemical property of Mylar, silicone rubber, butyl rubber and, to a lesser extent, Kel-F. Teflon apparently withstands the exposure without severe alteration as indicated by weight change and visual and manual examination. Thus, it is not recommended that the above materials other than Teflon be used in these systems. Teflon should not be used indiscriminately.

TEST SCHEMATIC

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SWITCH

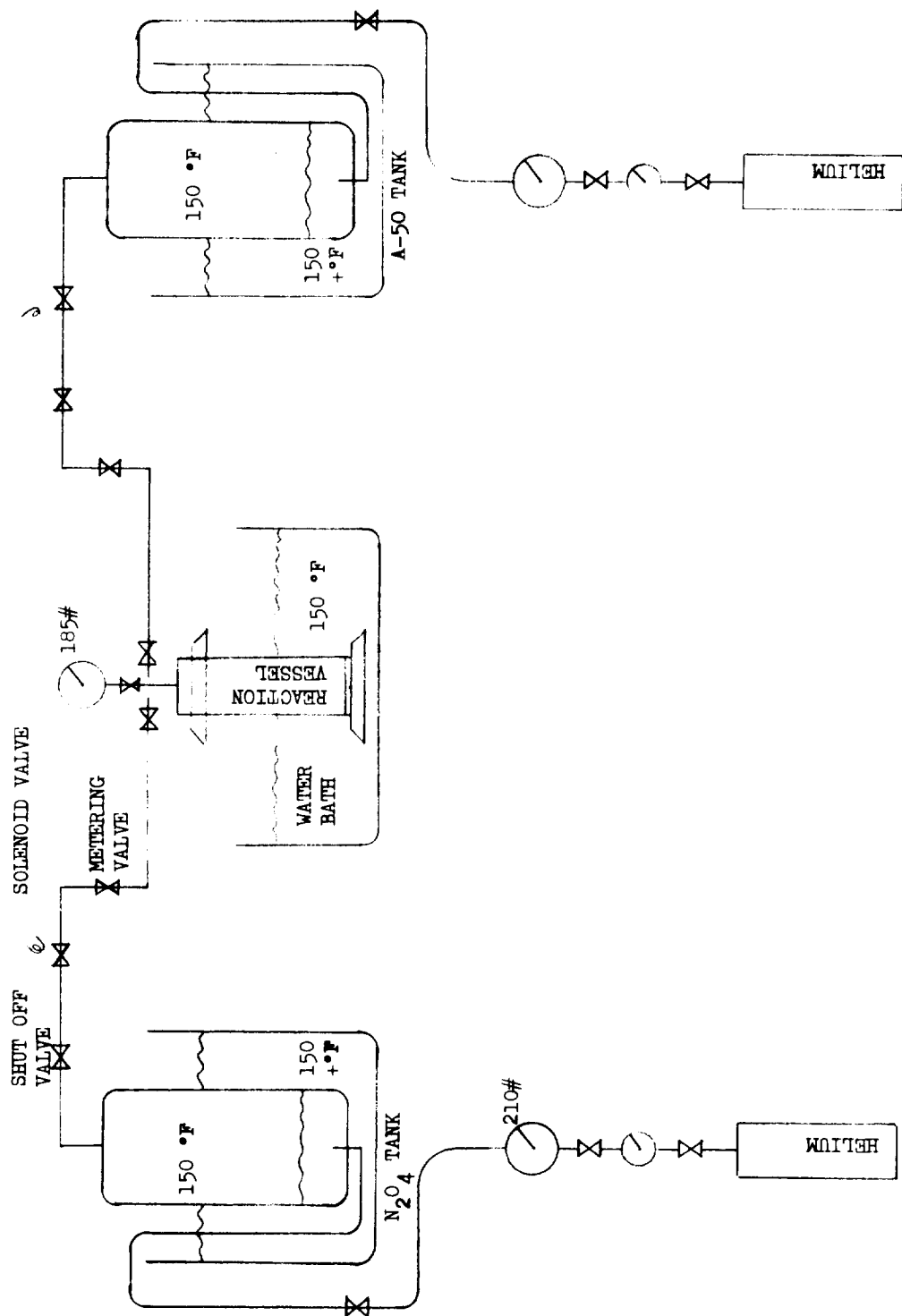


FIGURE 1

TABLE I

TEST PRESSURE AND TEMPERATURE DATA

RUN NO.	REACTION VESSEL INITIAL PRESSURE psig	REACTION VESSEL FINAL PRESSURE psig	REACTION VESSEL INITIAL TEMP. °F.	REACTION VESSEL FINAL TEMP. °F.	TEMPERATURE DIFFERENTIAL °F.
1	0	47	68	104	36 rise
2	0	165	74	121	47 rise
3	0	180	63	117	54 rise
4	0	195	72	125	53 rise
5	0	57	151	176	25 rise
6	0	166	149	206	54 rise
7	0	185	150	237	87 rise
8	0	200	149	250	101 rise

The following runs (9-16) are duplicates of runs 1-8 in sequence

9	0	45	65	108	43 rise
10	0	168	67	108	41 rise
11	0	182	66	114	48 rise
12	0	197	71	125	54 rise
13	0	62	145	170	25 rise
14	0	169	149	190	41 rise
15	0	183	145	200	55 rise
16	0	200	145	210	65 rise

The following two duplicate runs were control runs designed to determine temperature differential when helium only was used as the pressurant gas.

CONTROL TEST

1	0	163	70	98	28 rise
2	0	161	70	104	34 rise

TABLE II

TEST SPECIMEN DATAONE DAY TEST

<u>MATERIAL</u>	<u>WEIGHT GAIN OR LOSS (%)</u>	<u>WATER QUENCHED</u>	<u>THICKNESS IN INCHES</u>		<u>VISUAL OBSERVATIONS</u>
			<u>BEFORE</u>	<u>AFTER</u>	
Mylar	+12.68	yes	.0135	.015-.016	Very brittle, striated, broke easily.
Mylar	+13.61	no	.0135	.016-.017	Same as above
Teflon	+ 0.30	yes	.065	.065-.066	Very slight yellowing
Teflon	+ 0.28	no	.065	.065-.066	Very slight yellowing
Kel-F	+ 3.62	yes	.005	.0055	Curled somewhat
Kel-F	+ 3.86	no	.005	.0055	Curled somewhat
Silicone Rubber	- 2.33	yes	.018	.018	Wrinkled slightly
Silicone Rubber	- 2.79	no	.018	.0175	Wrinkled slightly

FIVE DAY TEST

Mylar	shattered	yes	.0135	.017	Very brittle, shattered
Mylar	shattered	no	.0135	.0175	Very brittle, shattered
Teflon	+ 0.41	yes	.064-.065	.064-.065	Yellowed and darkened somewhat
Teflon	+ 0.46	no	.064-.065	.065-.066	Yellowed and darkened somewhat
Kel-F	- 1.34	yes	.010	.011	Yellowed slightly and curled
Kel-F	+ 1.49	no	.010	.010	Yellowed slightly and curled
Silicone Rubber	-12.96	yes	.018	.017-.018	Curled on corners
Silicone Rubber	-13.44	no	.018	.0165	Curled on corners

TEN DAY TEST

Mylar	+ 7.49	yes	.0135	.017	Very brittle, striated
Mylar	+ 8.98	no	.0135	.017	Very brittle, striated
Teflon	- .004	yes	.067	.068	Very slightly darkened
Teflon	- .34	no	.067	.068	Very slightly darkened
Kel-F	+ 1.14	yes	.007	.0075	Curled and slightly darkened
Kel-F	+ 1.78	no	.007	.0075	Same as above
Butyl rubber	--	yes	.106	--	Very sticky, lost elasti- city, unable to remove
Butyl rubber	--	no	.109	--	all material from reac- tion vessel
Silicone rubber	-31.09	yes	.018	.021	Brittle, broke easily
Silicone rubber	-27.76	no	.018	.021	Brittle, broke easily